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§1.132 Amended Declaration of Ward T. Brown, May 1 2007. Serial No. 10/730,353.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No.: A01474

Applicant: Ward T. Brown *et al.*

Group Art Unit: 1714

Serial No.: 10/730,353

Filed: December 8, 2003

Examiner: Callie E. Shosho

For: Pigmented Polymer Composition

AMENDED DECLARATION OF WARD T. BROWN  
PURSUANT TO 37 C.F.R. §1.132

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This Amended Declaration, dated May 1, 2007 supercedes and replaces the earlier dated Declaration of April 4, 2007.

Sir:

I, Dr. Ward T. Brown, of North Wales, PA, declare and state:

1. I have a Ph.D in Physical Chemistry from the University of California at Berkeley. I have been employed by Rohm and Haas Company, Spring House Technical Center, 727 Norristown Road, Spring House, PA 19477 for over 18 years. During that period of time, I have been engaged in research in the field of polymer chemistry, including acrylic emulsion polymers and I have been active in the field of emulsion polymerization of phosphorus containing monomers for many years. My current position at Rohm and Haas is Distinguished Scientist. I am an inventor on more than 20 issued US patents, and I am a named co-inventor for the above-referenced application ("the '353 application").

2. The claims of the '353 application recite polymer compositions comprising

organic colorant particles and polymer particles comprised of polymerized units of phosphorus acid monomer, wherein the polymer particles have first phosphorus acid groups, such that

i) the polymer particles are prepared by aqueous emulsion polymerization of said phosphorus acid monomer at a pH of less than 2, or

ii) the polymer composition comprises a level of water soluble polymer having second phosphorus acid groups defined by ratios of equivalents of second phosphorus acid groups to equivalents of first phosphorus acid groups in the range of less than or equal to 1.5

The present invention seeks to solve the problem wherein polymerization of phosphorus acid monomers fails to incorporate all of the phosphorus acid monomers into the growing polymer particle and most of the polymerization of these monomers occurs in the aqueous phase instead of in the growing polymer particle. See, for example, the instant specification at page 11, lines 14-28.

3. I have read the Office Actions and the Advisory Action of February 26, 2007 and understand that instant claim 18 stands rejected under 35 U.S.C. §102(b) as being anticipated by Ma *et al.* (U.S. 6,247,808), that instant claims 18 and 19 stand rejected under 35 U.S.C. §102(e) as being anticipated by Dersch *et al.* (U.S. 6,492,451) and that instant claims 1-4, 6, 8-10, and 18-19 stand rejected under 35 U.S.C. §102(e) as being anticipated by Edwards *et al.* (U.S. 7,101,921). Further, I understand that the instantly recited level of water soluble polymers having second phosphorus acid groups is not disclosed, taught, suggested or inherent in any of the art references. Further, the references fail to state that the polymerizations were run at a pH of less than 2.

4. The Advisory Action of February 26, 2007 alleges that the Applicants have provided no evidence that in the art of Dersch *et al.*, Ma *et al.* and Edwards *et al.* more phosphorus acid monomer is polymerized in the aqueous phase than is instantly recited. In response to the Advisory Action, I have shown below that the amount of phosphorus acid monomer polymerized in the polymer particle of the cited art is such that the ratio of

phosphorus acid groups in a water soluble polymer to phosphorus acid groups in the polymer particle exceeds 1.5; and, thus, in the cited art, the amount of water soluble polymer from phosphorus acid monomer lies outside the instantly claimed range. Under my direction, the closest described polymerization from the closest prior art reference (Dispersion D1 of Dersch *et al.*) was repeated as closely as possible and analyzed for quantities of second phosphorus acid groups in the aqueous phase. Dispersion D1 was selected from Dersch *et al.*, because better incorporation into the polymer is generally seen for lower levels of phosphorus acid monomer charged. This is because the acid monomer is a negatively charged species when the polymerizations are run at a pH above the pKa of the acid monomer, as is the case in Dersch. When attempting to polymerize a negatively charged species, the greater the amount added, the harder it is to get the monomer into the negatively charged latex polymer particle. There were two differences between the repeat experiment and the experimental procedure described in D1 of Dersch *et al.* First, the preformed polymer seed that was used to start the polymerization was a 60 nm MMA/BA seed in place of a 30 nm p-STY seed, due to lack of availability of the 30 nm p-STY seed. It is known that this difference in seed particle size does not affect the polymerization or the incorporation of any specific monomer involved in the emulsion polymerization. Second, the experiment used the same wet adhesion promoter molecule as described in Dersch *et al.*, but, again due to availability, used a version from a different supplier. This change does not affect the polymerization or the incorporation of the phosphorus acid monomer. The aqueous phase of the resulting emulsion polymer latex was analyzed for phosphorus-containing monomer by  $P^{31}$  NMR (referenced using a calibration standard of disodium salt of polyvinyl phosphonic acid, and an internal marker solution of disodium phosphate). The error in the NMR integration of the area under the peaks of the NMR trace that represents the phosphorus-containing species in solution, ranges on the order of 10% or less and in no way compromises the conclusion of the experiment.

5. The emulsion polymerization details and the subsequent analysis are set forth below. To prepare Dispersion D1 of US 6,492,451 B1, I directed the following procedure which was, unless otherwise indicated, performed at standard temperature and pressure:

Charge 234 g of DI water, 38 g of a 5% sodium pyrophosphate solution and 3.66 g of a 60 nm BA/MMA seed latex (1.52 g solids) to a kettle and heat to 85°C under an N<sub>2</sub> atmosphere. Add 7.24 g of initial NaPS solution. Add monomer emulsion (ME) over 3 hours at 6.3 g /min, concurrently with the remaining NaPS solution (@ 0.27 g/min), and then continue to feed remaining NaPS solution over another hour @ 0.27 g/min.

When the initiator solution is complete hold temp at 85°C for 1 hour. Cool to 60°C.

At 60°C feed Chaser catalyst and Chaser activator to the kettle via separate feeds and maintain the batch at 60°C for one hour. Cool to room temperature, adjust pH to ~7.4 with 10% NaOH and filter.

### COMPOSITION -

Monomer Mix 56.7 BA / 40.2 MMA / 1.1 VPA / 2.0 AEEUM

NaPS = 0.27% B.O.M. (based on monomer)

Dowfax™ 2A1 = 1.07% B.O.M.

Disponil™ FES-77 = 1.61% B.O.M.

<u>CHARGE</u>	<u>KETTLE</u>	
MONOMER EMULSION		(pbw)
DI Water	234	193.7
Emulsifier #1 (45%) Dowfax 2A1	-	21.11
Emulsifier #2 (30%) Disponil Fes - 77	-	47.50
BA	-	502.5
MMA	-	356.3
Vinylphosphonic acid	-	10.2
AEEUM	-	<u>25.7</u>
(methacrylamidoethylethylene urea) (70% solids)		
<u>Total</u>	-	1157.0
DI water rinse		40

**BUFFER**

Sodium pyrophosphate (5% in water) 38.0  
(Tetra sodium diphosphoric acid)

**SEED LATEX (1.52 g solids)**

E-2086 (41.5%) / DI rinse 3.66 / 10

**INITIATOR SOLUTION**

NaPS / DI water 2.38 / 70.0

**CHASER CATALYST**

t-BHP (70%) / DI water 1.36 / 5.0

**CHASER ACTIVATOR**

Sodium bisulfite / DI water 0.95 / 6.3

**NEUTRALIZER**

NaOH (10%) to pH 7.2 65.0

**TOTALS Batch (pbw) ~1634**

**Monomer .887**

**Solids 924.0**

**% Solids 56.5**

The analysis of incorporated vinyl phosphonic acid was conducted, as follows:

Two 32.4ml centrifuge tubes (Beckman Optiseal #361625) were filled with the emulsion polymer (56.5% solids; 1.104% vinyl phosphonic acid on latex solids) and spun down at 50K RPM for 2hrs at 20°C (Sorvall Discovery 100). A 10.00g amount of the serum phase was removed, combined with 0.25g of 10% NaOH, and 8.25g of liquid was removed by evaporation to concentrate the sample. A calibration sample was made by diluting 0.0650g of an 18.37% solids water solution of polyvinyl phosphonic acid, disodium salt, to a total weight of 1.00g with water. A marker solution was made by dissolving 0.10g disodium phosphate in 3.50g D<sub>2</sub>O. A 1.00g amount of marker solution was added to both the concentrated serum sample and the calibration sample, then P<sup>31</sup>-NMR (128 scans, decoupled, Bruker Ultrashield 500) spectra were acquired for both the

concentrated serum sample and the calibration sample. The peaks (polyvinyl phosphonic acid, sodium salt 10.8ppm, sodium phosphate 2.7ppm) were integrated, with the integral for the sodium phosphate marker peak set equal to 100. The results obtained were:

<u>Sample</u>	<u>2.7ppm</u>	<u>10.8ppm</u>
Calibration	100	21.74
Serum	100	365.03

The ratio of second phosphorus acid groups (serum phase) to first phosphorus acid groups (latex incorporated) is calculated as follows:

Wt of polyvinyl phosphonate in calibration sample:  $0.0650 \times 0.1837 = 0.01194\text{g}$

Wt of polyvinyl phosphonate in 10g serum (second phosphorus acid groups):

$0.01194\text{g} \times (365.03 / 21.74) = 0.2005\text{g}$

Wt of emulsion polymer that contains 10g of serum:  $10\text{g} / (1 - 0.565) = 22.99\text{g}$

Wt of polyvinyl phosphonic acid charged in 22.99g of polymer emulsion:

$22.99\text{g} \times 0.565 \times 0.01104 = 0.1434\text{g}$ .

Wt of polyvinyl phosphonate corresponding to 0.1434g of polyvinyl phosphonic acid:

$0.1434\text{g} \times (154.03\text{g/mole} / 108.03\text{g/mole}) = 0.2044\text{g}$

Wt of incorporated polyvinyl phosphonic acid (first phosphorus acid groups):

$0.2044\text{g} - 0.2005\text{g} = 0.00396\text{g}$

**Ratio of second phosphorus acid groups to first phosphorus acid groups:**

$0.2005\text{g} / 0.00396\text{g} = 50.6$

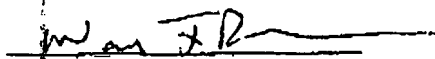
6. As shown in the results of the experiment, essentially all of the charged phosphorus acid monomer ends up in the form of a water soluble species in the aqueous phase, and very little is incorporated into the polymer particle. Accordingly, the ratio of equivalents of second phosphorus acid groups to equivalents of first phosphorus acid groups ranges far above the instantly recited 1.5:1, even taking the maximum NMR integration error into account. Therefore, there is very little incorporation of the phosphorus acid monomer into the growing polymer particle in the polymerizations of Dersch *et al.*

7. The experimental procedure from Dersch *et al.*, reproduced above, represents the

only art in which any example includes a phosphorus acid monomer, as instantly recited. Edwards *et al.* and Ma *et al.* each fail to exemplify use of phosphorus acid monomer. Ma *et al.* fail to show any polymerization example at all. It should be noted that the factors that control incorporation of the phosphorus acid monomers are the same in both one-stage and two-stage polymerizations. Thus, performing the emulsion polymerization as a multistage polymerization, as described in Edwards, does not affect the ratio of equivalents of second phosphorus acid groups to equivalents of first phosphorus acid groups. Phosphorus acid monomers in the first stage monomer emulsion do not get a second chance for incorporation during the second stage polymerization; they are either incorporated into the growing latex polymer particle or they polymerize in the aqueous phase to give water soluble polymers. The latter do not have sites of unsaturation and are not polymerized into the latex particle. Phosphorus acid monomers in the second stage monomer emulsion experience no different scenario to that of a one-stage polymerization. Accordingly, the instant claims recite an invention which provides an unexpectedly large amount of phosphorus acid monomer incorporated in the disperse particle polymer in comparison to the closest art cited in the rejections; and the instant claims are thus not obvious over any of Dersch *et al.*, Ma *et al.* and Edwards *et al.* Further, the instant claims recite an invention that is not inherent in the art of Dersch *et al.*, Ma *et al.* and Edwards *et al.*

8. I declare that all statements made in this declaration of my own knowledge are true. I believe that all statements made herein on information and belief also are true. Furthermore, I understand that willful false statements and the like so made are punishable by fine or imprisonment, or both, under the United States Code, and such willful false statements may jeopardize the validity of any patent application or patent that may issue on this patent application.

Date: MAY 1, 2007



Dr. Ward T. Brown